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APPLICATION FOR LETTERS PATENT

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**Particle Forming Method, Laser Pyrolysis Particle
Forming Method, Chemical Mechanical Polishing
Slurry, And Chemical Mechanical Polishing Process**

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1 Particle Forming Method, Laser Pyrolysis Particle Forming Method,
2 Chemical Mechanical Polishing Slurry, And Chemical Mechanical
3 Polishing Process

4 TECHNICAL FIELD

5 This invention relates to particle forming methods, laser pyrolysis
6 particle forming methods, to chemical mechanical polishing slurries, and
7 to chemical mechanical polishing processes.
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10 BACKGROUND OF THE INVENTION

11 Chemical mechanical polishing is one technique utilized to process
12 the outer surface of various layers formed over a semiconductor wafer.
13 One principal use of chemical mechanical polishing is to render an
14 outer wafer surface of a layer or layers to be more planar than existed
15 prior to starting the polishing. Only some or all of the outermost layer
16 being polished might be removed during such a process.

17 In chemical mechanical polishing, both the wafer and the pad
18 which polishes the wafer are typically caused to rotate, typically in
19 opposite directions during the polishing action. A liquid slurry is
20 received intermediate the wafer and the polishing pad. The slurry
21 comprises a liquid solution, typically basic, and a solid abrasive grit
22 material, typically constituting particles of a consistent size (i.e., within
23 5 nanometers of a typical selected size from around 25 to 100
24 nanometers in diameter). The action of the liquid solution and abrasive

1 grit within the slurry intermediate the wafer pad and wafer imparts
2 removal of outer wafer layers utilizing both chemical and mechanical
3 actions.

4 One particular goal in the development of chemical mechanical
5 polishing slurries is the provision of particles of substantially uniform
6 size. As identified above, the typical individual particle size of chemical
7 mechanical polishing slurries is less than about 100 nanometers.
8 Manufactured materials of this fine size are commonly referred to as
9 nanomaterials or nanoparticles. Such materials find use in polishing
10 processes and materials other than chemical mechanical polishing, for
11 example in batteries and in chemical reaction catalysts. Such materials
12 have historically been fabricated using combustion flame synthesis
13 methods, such as for example described in U.S. Patent No. 5,876,683 to
14 Glumac et al. More recently, laser synthesis of nanoparticles is also
15 gaining interest, such as described in U.S. Patent No. 5,695,617 to
16 Graiver et al., *Laser Synthesis of Nanometric Silica Powders*, by M. Luce
17 et al., and *Synthesis of Polymerized Preceramic Nanoparticle Powders by*
18 *Laser Irradiation of Metalorganic Precursors*, by P.R. Strutt et al., which
19 are hereby incorporated by reference.

20 It would be desirable to improve upon the laser synthesis
21 methods, and to produce improved chemical mechanical polishing slurries
22 independent of the method fabrication.
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SUMMARY

The invention comprises particle forming methods including laser pyrolysis particle forming methods, chemical mechanical polishing slurries, and chemical mechanical polishing processes. In but one preferred implementation, a laser pyrolysis particle forming method includes feeding a first set of precursors to a first laser application zone. Laser energy is applied to the first set of precursors in the first laser application zone effective to react and form solid particles from the first set of precursors. Application of any effective laser energy to the solid particles is ceased and the solid particles and a second set of precursors are fed to a second laser application zone. Laser energy is applied to the second set of precursors in the second laser application zone effective to react and form solid material about the solid particles from the second set of precursors.

In one implementation, a particle forming method includes feeding a first set of precursors to a first energy application zone. Energy is applied to the first set of precursors in the first energy application zone effective to react and form solid particles from the first set of precursors. Application of any effective energy to the solid particles is ceased and the solid particles and a second set of precursors are fed to a second energy application zone. Energy is applied to the second set of precursors in the second energy application zone effective to react and form solid material about the solid particles from the second

1 set of precursors. Preferably, at least one of the first and second
2 applied energies comprises laser energy.

3 In one implementation, a chemical mechanical polishing slurry
4 comprises liquid and abrasive solid components. At least some of the
5 abrasive solid component comprises individually non-homogeneous abrasive
6 particles.

7 In one implementation, a chemical mechanical polishing process
8 includes rotating at least one of a semiconductor substrate and polishing
9 pad relative to the other. A chemical mechanical polishing slurry is
10 provided intermediate the substrate and pad, and the substrate is
11 polished with the slurry and pad during the rotating. The chemical
12 mechanical polishing slurry comprises liquid and abrasive solid
13 components. At least some of the abrasive solid component comprises
14 individually non-homogeneous abrasive particles.

15 BRIEF DESCRIPTION OF THE DRAWINGS

16 Preferred embodiments of the invention are described below with
17 reference to the following accompanying drawings.

18 Fig. 1 is a diagrammatic depiction of a laser pyrolysis particle
19 forming method in accordance with an aspect of the invention.

20 Fig. 2 is a diagrammatic sectional view of a chemical mechanical
21 polishing slurry abrasive particle.
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1 Fig. 3 is a diagrammatic representation of an alternate laser
2 pyrolysis particle forming method in accordance with an aspect of the
3 invention.

4 Fig. 4 is a diagrammatic view of an exemplary system used in a
5 chemical mechanical polishing process in accordance with an aspect of
6 the invention.

7 8 9 DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

10 This disclosure of the invention is submitted in furtherance of the
11 constitutional purposes of the U.S. Patent Laws "to promote the
12 progress of science and useful arts" (Article 1, Section 8).

13 A laser pyrolysis particle forming method is indicated generally
14 with reference numeral 10. Such comprises a reaction flow path 12
15 having a beginning end 14 and a product collection end 16. Reaction
16 flow path 12 comprises at least first and second spaced laser application
17 zones 18 and 20, respectively. A pair of first precursor inlets 22 and
18 24 are provided to reaction flow path 12 proximate beginning end 14
19 in advance of first laser application zone 12. A pair of second
20 precursor inlets 26 and 28 are provided to reaction flow path 12
21 between first laser application zone 18 and second laser application
22 zone 20. A pair of inert gas inlets 30 and 32 are also provided
23 intermediate first laser application zone 18 and second laser application
24 zone 20. Such are preferably provided for injection of purging gas at

1 this point in the flow path, as will be described below. More or fewer
2 precursor or inert inlets could of course be provided.

3 Reaction flow path end 16 includes a suitable trap 34 for
4 collecting the formed particles. Unreacted precursor material, purge
5 and/or carrier gases are expelled via an exhaust 36.

6 At least one precursor is fed through one of first inlets 22 and
7 24 to reaction flow path 12 in advance of first laser application
8 zone 18. The precursor or precursors are preferably provided as a gas.
9 In a particular example, where for example SiO_2 particles are to be
10 formed, example reactive flow gases for lines 22 and 24 include a silane
11 such as dichlorosilane, and O_2 , respectively. An example flow rate
12 range for the dichlorosilane is from about 100 sccm to about 10 slm,
13 with an example flow rate for the O_2 also being from about 100 sccm
14 to about 10 slm. Temperature and pressure are preferably maintained
15 within the reaction flow path outside of first and second spaced laser
16 application zones 18 and 20 such that reaction of gases therein does
17 not occur.

18 The one or more precursors fed from precursor inlets 22 and 24
19 are fed along reaction flow path 12 to first laser application zone 18.
20 The dichlorosilane and oxygen in this example comprise a first set of
21 precursors which is fed to first laser application zone 18. Laser energy
22 is applied in first laser application zone 18 effective to react and form
23 solid particles from the at least one precursor fed from at least one
24 of first inlets 22 and 24. An example preferred pressure is 200mTorr,

1 with preferred temperature being ambient and not controlled. The
2 particles formed are exemplified in Fig. 1 by the illustrated specks or
3 dots materializing in laser application zone 18. An example laser is the
4 commercial PRC-Oerlikon 1500W fast-axial-flow CO₂ laser, such as
5 described in the Luce et al. article referred to in the Background
6 section of this document. Other lasers, including excimer lasers, are
7 also of course utilizable, with KrF, ArF and Xe lasers being but only
8 three additional examples. Any suitable power can be chosen effective
9 to provide suitable energy to cause a reaction and produce particles,
10 and could be optimized by the artisan depending upon gas flow rate,
11 desired particle size, etc. The material of the particles formed utilizing
12 the example dichlorosilane and O₂ feed gases will predominately
13 comprise SiO₂.

14 Such provides but one example process of first applying laser
15 energy to a first set of precursors in a first laser application zone
16 effective to react and form solid particles from the first set of
17 precursors. Alternate processing is of course contemplated. For
18 example, and by way of example only, precursors could be injected as
19 liquid, and/or directly into the laser application zone as opposed to in
20 advance thereof as depicted and described relative to the most preferred
21 embodiment.

22 The formed solid particles and any unreacted gas are fed from
23 first laser application zone 18 along reaction flow path 12 to between
24 the first and second spaced laser application zones 18 and 20,

1 respectively. Such provides but one example of ceasing application of
2 any reaction effective laser energy to the solid particles after their
3 initial formation in first laser application zone 18. At least one
4 precursor is fed through at least one of second precursor inlets 26 and
5 28 into reaction flow path 12 between first and second laser application
6 zones 18 and 20 having the solid particles flowing therein.

7 The precursor or precursors fed from at least one of second
8 inlets 26 and 28 and the solid particles are fed along reaction flow
9 path 12 to second laser application zone 20. Such provides but one
10 example of feeding the solid particles and a second set of precursors
11 to a second laser application zone. Laser energy is applied in second
12 laser application zone 20 effective to react and form solid material
13 about the solid particles from the at least one precursor fed from at
14 least one of second inlets 26 and 28. Such is shown in Fig. 1 by the
15 enlarged or grown particles appearing within second laser application
16 zone 20.

17 The precursors provided from one or both of first inlets 22 and
18 24 can be the same as that provided from one or both of second
19 precursor inlets 26 and 28, effectively forming substantially homogeneous
20 solid particles at the conclusion of applying laser energy in second laser
21 application zone 20. In effect in this example embodiment, the first
22 formed particles in first laser application zone 18 are subsequently
23 coated in a separate laser application zone 20 with the same material,
24 effectively layering and growing particles which are substantially

1 individually homogeneous throughout. Application of at least two and
2 perhaps more laser pyrolysis steps for forming the particles might result
3 in more uniform size and shaped particles than might otherwise occur
4 in a single laser application process.

5 Alternately by way of example, the first and second sets of
6 precursors can be provided to be different, with the second depicted
7 laser energy application forming a solid material coating over the solid
8 particles which is different from material of the solid particles formed
9 in first laser application zone 18. Such might be utilized to provide
10 optimized solid particles having different property outer and inner
11 materials, for example making the outer coating material or materials
12 harder or softer than the inner or initial material of the solid particles
13 formed in first laser application zone 18.

14 By way of example only, and continuing with the above example
15 where SiO_2 particles are formed in first laser application zone 18, the
16 subsequently formed solid material coating the particles as formed in
17 second laser application zone 20 might comprise an elemental metal,
18 such as elemental tungsten. For example, one or more precursors could
19 be fed into reaction flow path 12 from multiple inlets 26 and 28 to
20 provide suitable reactive precursor materials, preferably in the form of
21 gases, for feeding to second laser application zone 20. For example,
22 a mixture of WF_6 and an effective amount of H_2 could be fed as a
23 mixture from each of inlets 26 and 28, which would react in second
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1 laser application zone 20 to coat the initially formed SiO_2 particles with
2 elemental tungsten.

3 Where the first and second sets of precursors are different, it
4 might be desirable to provide an inert purge gas, such as N_2 or Ar,
5 from inlets 30 and 32 between first and second laser application
6 zones 18 and 20 in advance of precursor inlets 26 and 28. Such
7 purging might be desired to effectively dilute any unreacted remaining
8 gases which have flowed through first laser application zone 18 to
9 prevent reaction of the same in second laser application zone 20 where
10 one or more discrete different material coatings are desired on the
11 outside of the initially formed particles. Such gases flowing from first
12 laser application zone 18 and any purged gases injected by inlets 30
13 and 32 might be exhausted (not shown) from reaction flow path 12 in
14 advance of subsequent precursor injection at at least one of 26 and 28,
15 or alternately flow in a diluted manner through second laser application
16 zone 20.

17 The first and second sets of precursors might or might not share
18 at least one common precursor. The above described example is one
19 where no precursor material is common to the first and second sets.
20 Consider alternately by way of example only a process wherein it is
21 desired to form inner and outer layers of a particle which comprise
22 different nitrides. For example, consider forming the inner layer to
23 comprise TiN, and forming the outer layer to comprise a harder WN
24 material. NH_3 could be utilized as one of the precursor gases for

1 supplying the nitrogen component of the formed nitrides in both the
2 first and second sets of precursors. In one example, an abundance of
3 NH_3 could be fed to reaction flow path 12 in advance of first laser
4 application zone 18. An example additional first precursor gas flowing
5 from one or both of first inlets 22 and 24 would be TiCl_4 . The TiCl_4
6 and NH_3 would desirably react to form TiN particles in first laser
7 application zone 18. Unreacted NH_3 and reaction byproducts would
8 flow from first laser application zone 18, and could be combined with
9 WF_6 flowing out of one or both of second inlets 26 and 28. The
10 WF_6 and NH_3 would desirably react within second laser application
11 zone 20 to form an outer coating of WN over the initially formed TiN
12 particles. Additional NH_3 might be added to reaction flow path 12
13 intermediate first laser application zone 18 and second laser application
14 zone 20 through one or both of inlets 26 and 28.

15 More than two laser application zones or laser applications might
16 also be utilized. Regardless, the processes most preferably are utilized
17 to produce nanomaterials, whereby the ultimately formed solid particles
18 have a maximum diameter of no greater than 1 micron, and more
19 preferable no greater than 100 nanometers.

20 Fig. 2 depicts an individually formed non-homogeneous particle 50.
21 Such comprises an inner exemplary portion 52 formed within first laser
22 application zone 18, and an outer coating 54 formed in second laser
23 application zone 20.
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1 The resultant formed particles are collected in trap 24 (Fig.1),
2 with remaining precursor inert or carrier gases being exhausted via
3 line 36 Fig. 1.

4 The above described processing depicted the first and second laser
5 application zones as being different and spaced from one another along
6 a reaction flow path. Alternate considered processing in accordance
7 with the invention is shown in Fig. 3, whereby the first and second
8 laser application zones comprise the same zones in different first and
9 second applications of laser energy to the same or different precursors.
10 Like numerals from the first described embodiment are utilized where
11 appropriate, with differences being indicated with the suffix "a", or with
12 different numerals.

13 Method 10a in Fig. 3 differs from that depicted in Fig. 1 by
14 provision of a single laser application zone 18, and provision of a
15 recycle stream 60 from trap 34 back to immediately in advance of laser
16 application zone 18. In a preferred process in accordance with the
17 Fig. 3 methodology, particles would initially be formed and collected in
18 trap 34. Thereafter, the particles would be flowed back to reaction
19 flow path 12a in advance of laser application zone 18, preferably in one
20 or more discrete single batches for uniformity in size control, and
21 combined with the same or different precursors for subsequent coating
22 thereof. Further alternately and less preferred, pulsed laser application
23 might occur in a single or multiple laser application zone(s) relative to
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1 one or more precursor gases to sequentially form multiple layered or
2 coated particles.

3 Also contemplated in accordance with aspects of the invention is
4 application of energy other than laser energy to effect some or all of
5 the particle formation. For example, one or both of energy application
6 zones 18 and 20 might comprise energy application sources other than
7 laser. By way of example only, such might include a combustion flame,
8 a plasma flame, photosynthesis such as UV light application, and other
9 heat energy such as passing the precursors/forming particles through a
10 pass-through furnace. Further, energy application zones 18 and 20
11 might comprise the same or different energy types.

12 The above described produced solid particles are preferably
13 utilized in forming a chemical mechanical polishing slurry at least a
14 portion of which contains such particles as the solid abrasive material
15 within the slurry. Thereby, a preferred chemical mechanical polishing
16 slurry in accordance with the invention comprises liquid and abrasive
17 solid components. At least some of the abrasive solid components
18 comprise individually non-homogeneous abrasive particles produced by the
19 above described or prior art or yet to be developed methods. Such
20 particles might be characterized by two distinct material layers or more
21 layers. Preferably, one of the two layers will envelop the other.

22 Slurries in accordance with the invention can be utilized in
23 chemical mechanical polishing processes in accordance with another
24 aspect of the invention, and as generally described with reference to

Fig. 4. An exemplary system shown in diagrammatic or schematic form for conducting a chemical mechanical polishing method in accordance with the invention is indicated generally with reference numeral 60. Such comprises a polishing table or platen 62 having a polishing pad 64 received thereatop. A wafer carrier 66 is juxtaposed in opposing relation relative to polishing pad 64. A workpiece 68, typically in the form of a semiconductor wafer, is received by wafer carrier 66. A slurry injection port 70 is positioned to emit fluid onto pad 64 to be received between pad 64 and wafer 68 during polishing. Wafer carrier 66 and polishing table 62 are typically mounted for independent controllable rotation relative to one another. One or more wafer carrier head assemblies might be utilized for a single polishing table, and be mounted for translational movement as well relative to table 62. The above describes but one very diagrammatic exemplary depiction of a chemical mechanical polishing system within which a method of the invention might be utilized.

In accordance with this aspect of a chemical mechanical polishing process in accordance with the invention, at least one of a semiconductor substrate and polishing pad are rotated relative to the other. A chemical mechanical polishing slurry is provided intermediate the substrate and pad, and the substrate is polished with the slurry and pad during the rotating. The chemical mechanical polishing slurry comprises liquid and abrasive solid components. At least some of the abrasive solid component comprises individually non-homogeneous abrasive

1 particles, such as for example described above and producible in
2 accordance with the inventive and other processes.

3 In compliance with the statute, the invention has been described
4 in language more or less specific as to structural and methodical
5 features. It is to be understood, however, that the invention is not
6 limited to the specific features shown and described, since the means
7 herein disclosed comprise preferred forms of putting the invention into
8 effect. The invention is, therefore, claimed in any of its forms or
9 modifications within the proper scope of the appended claims
10 appropriately interpreted in accordance with the doctrine of equivalents.
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